

# Dual functionality of formamidine polymers, as ligands and as bases, in ruthenium-catalysed hydrogen evolution from formic acid

Cite this: *Polym. Chem.*, 2013, **4**, 2741

Stephan Enthaler,<sup>\*a</sup> Henrik Junge,<sup>\*b</sup> Anna Fischer,<sup>\*a</sup> Anja Kammer,<sup>b</sup> Sebastian Krackl<sup>a,c</sup> and Jan Dirk Epping<sup>c</sup>

Received 23rd January 2013  
Accepted 20th February 2013

DOI: 10.1039/c3py00120b

www.rsc.org/polymers

In the present study, the ruthenium-catalysed decomposition of formic acid to yield hydrogen has been examined. A ruthenium complex modified polyformamidine network was used as a solid catalyst. As a dual support the polyformamidine acts both as a ligand and as a base for the activation of formic acid.

## Introduction

The creation of a hydrogen economy has been envisaged as a promising alternative for the current fossil fuel based energy feedstock.<sup>1</sup> In this regard, the use of molecular hydrogen as a secondary energy carrier yields energy and water as an environmentally friendly side product after decomposition in *e.g.*, a fuel cell.<sup>2</sup> However, so far various problems of the hydrogen economy have not been resolved. One of the major issues is the development of suitable hydrogen storage systems, since current systems display some difficulties (*e.g.*, tank systems: need for high-pressure or low temperature equipment; metal hydrides, polymers, amino boranes: low reversibility; metal organic frameworks: low temperature; biomass: social issues).<sup>3</sup> Promising chemical hydrogen storage systems, as studied recently, involve the transformation of carbon dioxide to formic acid and *vice versa* as well as carbonate or bicarbonate to formate.<sup>4,5</sup> Formic acid ( $\text{HCO}_2\text{H}$ ), a liquid at RT, can easily be approached by catalytic reduction of carbon dioxide with molecular hydrogen (Fig. 1), while the catalytic decomposition of formic acid to release the stored hydrogen only liberates carbon dioxide. As such formic acid is an interesting option for the convenient, reversible and environmental-friendly storage of hydrogen, allowing easy transport, handling and refueling compared to other methodologies.

Recently the evolution of hydrogen by catalytic decomposition of formic acid has been extensively studied in the presence

of homogeneous catalysts.<sup>6,7</sup> Especially ruthenium based catalysts have been demonstrated to be highly active for that purpose. In more detail, ruthenium complexes modified by nitrogen or phosphane ligands have been successfully applied in the evolution of hydrogen. However the presence of amines or other bases is essential in such homogeneous systems to force the reaction towards hydrogen production.<sup>8</sup> As such, beside the benefit in handling and recovering of supported ruthenium catalysts, the heterogenisation of those on polymeric supports, featuring both ligand and basic sites, could be a promising approach for hydrogen generation from formic acid and for improving the quality of hydrogen by the avoidance of amine contamination (Fig. 2).<sup>9</sup> Recently some of us studied the application of well-defined formamidine ligands in the iron-catalyzed oxidation of carbon carbon double bonds.<sup>10</sup> Especially polymeric formamidines could be used successfully as polymeric ligands for the iron-catalysed Friedel–Crafts alkylation.<sup>11</sup> Polymeric formamidines, due to their straightforward synthesis and great availability of the starting materials, can provide suitable and abundant coordination sites for metals and further act as appropriate basic sites.<sup>12</sup> Additionally, monomeric formamidines have been shown to be appropriate bases for hydrogen generation from formic acid.<sup>13</sup>

Herein, we report on our initial studies on the application of polyformamidine as dual ligand/basic supports in the

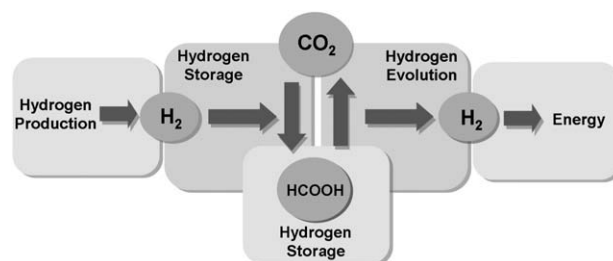


Fig. 1 Carbon dioxide/formic acid based hydrogen storage system.

<sup>a</sup>Technische Universität Berlin, Department of Chemistry, Cluster of Excellence "Unifying Concepts in Catalysis", Straße des 17. Juni 135/C2, D-10623 Berlin, Germany. E-mail: stephan.enthaler@tu-berlin.de; Fax: +49 3031429732; Tel: +49 3031422039

<sup>b</sup>Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, D-18059 Rostock, Germany. E-mail: henrik.junge@catalysis.de; Fax: +49 381128151174; Tel: +49 3811281174

<sup>c</sup>Technische Universität Berlin, Department of Chemistry, Metalorganics and Inorganic Materials, Technische Universität Berlin, Straße des 17. Juni 135/ C2, D-10623 Berlin, Germany

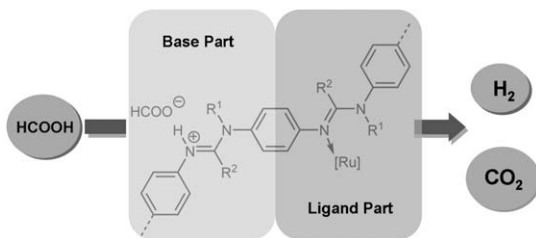


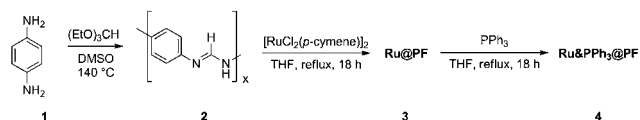
Fig. 2 Ligand-base concept for hydrogen evolution from formic acid.

ruthenium-catalysed hydrogen evolution by the decomposition of formic acid.

## Results and discussions

For the synthesis of polyformamidine the procedure was performed in accordance to the protocol reported by Böhme and co-workers with slight modifications.<sup>10</sup> A dimethylsulfoxide solution of *para*-phenylene diamine (**1**) and triethyl orthoformate was stirred at 140 °C for 24 hours under non-inert conditions (Scheme 1). After work-up a yellow-orange powder was obtained, which is highly stable up to a temperature of 300 °C. It is noteworthy that the compound is highly insoluble in various organic solvents (*e.g.*, DMSO, THF, toluene, CH<sub>2</sub>Cl<sub>2</sub>). For **2** <sup>13</sup>C{<sup>1</sup>H} CP/MAS NMR was applied, due the poor solubility, resulting in broad overlapping signals. Applying <sup>13</sup>C{<sup>1</sup>H} CP/MAS NMR we found for polyformamidine **2** a chemical shift of 146.4 ppm for the [N=C(H)–N] group, which is in agreement with well-defined formamidine ligands (*e.g.*, *N,N'*-bisphenylformamidine, <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>) δ = 149.5 ppm).<sup>14</sup> Additionally, with IR spectroscopic measurements for *N,N'*-bisphenylformamidine (1679 cm<sup>−1</sup>) and **2** (1660 cm<sup>−1</sup>) a shift of 19 cm<sup>−1</sup> for the band of the C=N functionality was detected. Furthermore, attempts to elucidate the molecular weight (MALDI TOF MS) of the polymeric compound failed due to the poor solubility.

In order to support ruthenium on the polyformamidine material, compound **2** was refluxed for 18 hours in THF with [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>. After the work-up a color change from yellow to red-brown of the polymer was observed. Moreover, phosphanes were reported to increase the reactivity of homogeneous hydrogen evolution catalysts, the Ru@PF **3** material was further refluxed in THF for 18 h in the presence of triphenylphosphane, leading to a phosphane doped compound **4** (Ru&PPh<sub>3</sub>@PF).<sup>6,7</sup> Applying <sup>13</sup>C{<sup>1</sup>H} CP/MAS NMR we found for **3** a resonance at 145.5 ppm and for **4** a resonance of 144.5 ppm, which are characteristics for the [N=C(H)–N] function. In comparison to the unmodified polymer **2** (δ = 146.4 ppm) the resonances are slightly shifted. In addition, compound **4**



Scheme 1 Synthesis of polyformamidine **2** and ruthenium supported on polyformamidine **2**.

was investigated by <sup>31</sup>P NMR showing a resonance at 33.4 ppm. These results indicate the coordination of the triphenylphosphane, since free triphenylphosphane resulted in a chemical resonance of −5.8 ppm. Furthermore, the obtained resonance is in agreement with well-defined ruthenium complexes containing triphenylphosphane and nitrogen based ligands.<sup>15</sup> In addition, IR measurements revealed a shift of the band at 1660 cm<sup>−1</sup> (C=N functionality of **2**) to 1663 cm<sup>−1</sup> for **3** and **4** (C=N functionality). The morphology of the obtained powders and the ruthenium distribution on the support prior to catalysis was investigated with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. Fig. 3 shows a representative SEM image of a [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> loaded polyformamidine powder particle. EDX mapping reveals that the ruthenium and the chlorine are well distributed over the polyformamidine particles. An atomic ratio (Cl : Ru) of 1.8 was determined, which is in agreement with the ratio of the starting ruthenium complex [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>. Moreover, a ruthenium to nitrogen ratio of 1 : 15 was found, which is in accordance to the loading conditions. On the other hand SEM measurements for Ru&PPh<sub>3</sub>@PF (**4**) showed no particular change of the particle morphology. Besides ruthenium and chlorine also phosphorous could be detected. As observed for the Ru@PF material **3** a homogeneous distribution of PPh<sub>3</sub> on

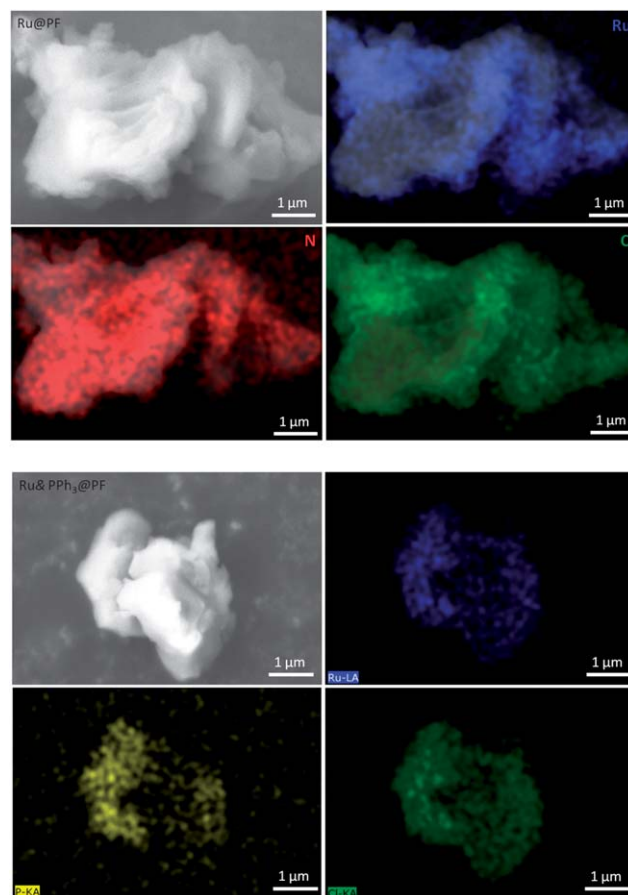


Fig. 3 SEM micrographs and EDX mapping of Ru@PF (**3**) and Ru&PPh<sub>3</sub>@PF (**4**) powders after synthesis and prior to catalysis.

the Ru@PF material was revealed by EDX mapping. Atomic ratios for Ru : Cl : P of 1 : 1.8 : 0.7 were determined. The obtained values revealed a possible coordination of one equivalent of triphenylphosphane per ruthenium. The additional coordination sites of the ruthenium are probably occupied by the polyformamidine ligand.

With the material in hand we became interested in the catalytic abilities in the decomposition of formic acid (Table 1). Three different Ru@PF materials with Ru contents ranging from 1.88 to 7.00 wt% Ru and one Ru&PPh<sub>3</sub>@PF (2.27 wt% Ru) sample have been tested. Therefore a double-walled thermostatically controlled reaction vessel was evacuated, heated, and purged with argon 10 times to remove any other gas, before the solvent dimethylformamide (DMF) and the substrate formic acid (FA) were poured in. The vessel was brought to the desired temperature (60 °C) and was kept constant at least for 30 min to reach equilibration. Then the reactions were started by addition of the ruthenium loaded polyformamidine in a Teflon crucible. The volume of evolved gases was quantitatively measured using automatic or manual gas burets.<sup>16</sup> In addition, gases were qualitatively and quantitatively determined by GC with a TCD. The conversion of formic acid is between 0.6 and 35% except for the upscale experiment (≥98%).

In all cases a 1 : 1 mixture of hydrogen : carbon dioxide was observed. Besides CO has been generated only in the ppm range, underlining the good selectivity of the applied catalysts.

[RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> is known to be an appropriate catalyst precursor for the hydrogen generation from a formic acid triethylamine mixture (5 : 2) (Table 1, entry 1). However, the activity drops significantly in the absence of the amine (Entry 2). The application of Ru@PF with 7.00 and 3.49 wt% ruthenium as a pre-catalyst results in almost similar low turnover numbers as obtained for the unsupported [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (Table 1, entries 3 and 4). However, the material with a Ru loading of 1.88 wt% shows a much better activity than applying 3.49 wt% as

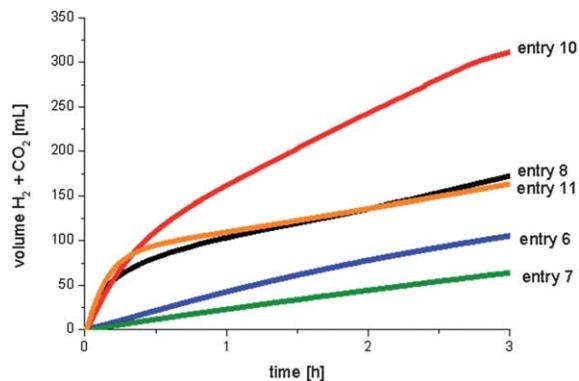
well as 7.00 wt% Ru (entries 5 and 6). A probable reason is the rising ratio of formamidine units to formic acid. Thus, as a secondary effect the lower ruthenium loading of the polyformamidine is accompanied by an increased number of *N*-containing moieties, which significantly improves the activity. This has been additionally proven by an experiment with further addition of unmodified 2 (entry 7). With raising the amount of basic sites of Ru@PF from 1 : 135 to 1 : 18 with respect to formic acid an increase of the turnover number by a factor of 1.6 was noticed (Table 1, entries 4 and 7). This is consistent with a previous report concerning the influence of the base amount on the activity.<sup>13</sup> Further addition of unmodified 2 resulted only in a slight increase of the activity. Moreover, both systems, [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> as well as Ru@PF, were tested in the presence of catalytic amounts of triphenylphosphane as ligand. Here an improved turnover number of 206 (3 h) was attained for the Ru@PF material (Table 1, entry 8). When both the ruthenium complex and phosphane are immobilized on PF in a ratio of 1 : 1.23 less catalytic activity is obtained (entry 9). However its performance could be significantly improved by further addition of 1.77 equiv. of PPh<sub>3</sub> resulting in an Ru : P ratio of 1 : 3 (Entry 10). It is noteworthy that this is a higher activity than it was found for the unsupported [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>/PPh<sub>3</sub> with NEt<sub>3</sub> addition (entry 11). Furthermore, in Fig. 4 the comparison of the gas evolution experiments is shown within the investigated time-frame. As seen in the figure in the first 20 min a high catalytic activity was observed for Ru@PF modified by PPh<sub>3</sub> compared to the unmodified pre-catalyst, while afterwards the slope is almost comparable for both systems except for 2.27 wt% Ru&PPh<sub>3</sub>@PF/1.77 equiv. PPh<sub>3</sub> which is still more active.

On the basis of the promising results we were prompted to perform an upscaling experiment. Therefore, we applied 100 μmol Ru (2.27 wt% Ru&PPh<sub>3</sub>@PF) and additional 1.77 equiv. of PPh<sub>3</sub>.

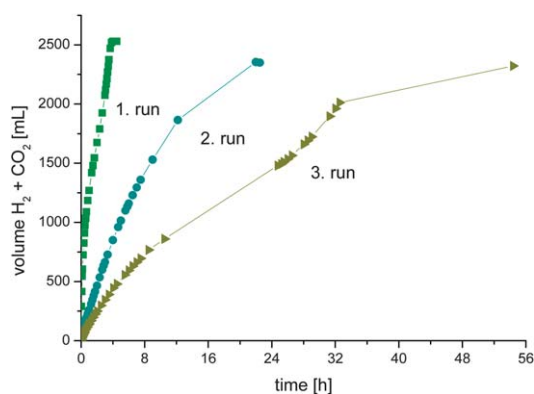
**Table 1** Ru@PF-catalysed decomposition of formic acid

$\text{HCOOH} \xrightarrow[\text{DMF, 60 } ^\circ\text{C}]{\text{supported [Ru]-catalyst}} \text{H}_2 + \text{CO}_2$				
Entry <sup>a</sup>	Pre-catalyst	<i>n</i> Ru [μmol]	V (3 h) [mL]	TON <sup>b</sup> (3 h)
1 <sup>c</sup>	[RuCl <sub>2</sub> ( <i>p</i> -cymene)] <sub>2</sub>	19.1	904	969
2 <sup>d</sup>	[RuCl <sub>2</sub> ( <i>p</i> -cymene)] <sub>2</sub>	19.1	35	37
3 <sup>d</sup>	7.00 wt% Ru@PF	13.9	22	33
4 <sup>d</sup>	3.49 wt% Ru@PF	13.3	30	46
5 <sup>d</sup>	1.88 wt% Ru@PF	13.9	77	114
6 <sup>d</sup>	1.88 wt% Ru@PF	19.1	103	110
7 <sup>e</sup>	3.49 wt% Ru@PF	17.9	63	72
8 <sup>f</sup>	3.49 wt% Ru@PF/3PPh <sub>3</sub>	17.9	180	206
9 <sup>d</sup>	2.27 wt% Ru&PPh <sub>3</sub> @PF	19.1	16	17
10 <sup>g</sup>	2.27 wt% Ru&PPh <sub>3</sub> @PF/1.77 equiv. PPh <sub>3</sub>	19.1	303	325
11 <sup>c</sup>	[RuCl <sub>2</sub> ( <i>p</i> -cymene)] <sub>2</sub> /3PPh <sub>3</sub>	19.1	158	169

<sup>a</sup> General conditions: reaction time 3 hours at 60 °C. <sup>b</sup> TON = turnover number, corresponds to the ruthenium loading. <sup>c</sup> DMF (5.0 mL) and HCOOH/NEt<sub>3</sub> (5 : 2) (5.0 mL). <sup>d</sup> DMF (8.0 mL) and HCOOH (2.0 mL). <sup>e</sup> DMF (8.0 mL), HCOOH (2.0 mL), and addition of unmodified 2 resulting in HCOOH : 2 18 : 1. <sup>f</sup> 57.3 μmol PPh<sub>3</sub>, DMF (8.0 mL) and HCOOH (2.0 mL). <sup>g</sup> 33.8 μmol PPh<sub>3</sub> added, Ru : P = 1 : 3, DMF (8.0 mL), and HCOOH (2.0 mL).



**Fig. 4** Comparison of the gas evolution experiments (number refer to entries in Table 1).

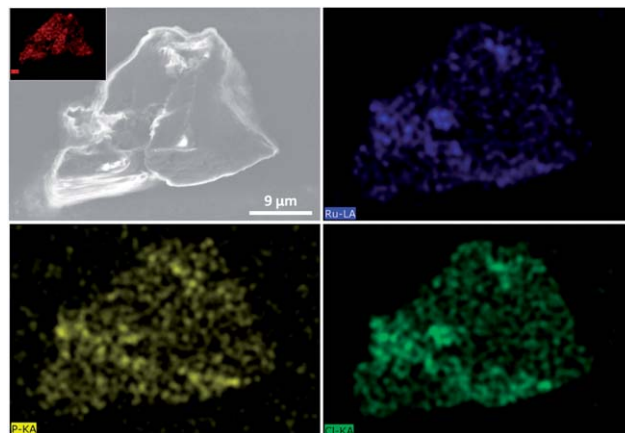


**Fig. 5** Up-scaling experiment with 2.27 wt% Ru&PPh<sub>3</sub>@PF/1.77 equiv. PPh<sub>3</sub>, [100 μmol Ru; 300 μmol triphenylphosphane; HCOOH (2.0 mL), DMF (8.0 mL), 60 °C; restart by addition of 2 mL of HCOOH, gas measured with a manual burette and analyzed by GC (H<sub>2</sub> : CO<sub>2</sub> 1 : 1, CO : <10 ppm)].

In the first run almost full conversion has been achieved within 4 hours (Fig. 5). After reaching 98% conversion (2530 mL H<sub>2</sub> + CO<sub>2</sub>, TON 518) the reaction has been restarted two times by further addition of 2 mL HCOOH (0.053 mol). In the second and third run 90% conversion has been achieved after 22 h and 46 h, respectively.

After another upscaling experiment applying 7.00 wt% Ru@PF (180 μmol Ru) and 287 μmol PPh<sub>3</sub> (Ru : PPh<sub>3</sub> 1 : 1.6) the solid catalyst was separated from the solvent and investigated again. The ruthenium loading of the most active material was evaluated by EDX (Fig. 6). The determined atomic ratios for Ru : Cl : P are 1 : 2 : 1.5, indicating on the one hand a slight leaching of the ruthenium during the catalysis (as confirmed by the decreased Ru : N ratio) and on the other hand a potential reorganization in the surface immobilized ruthenium. It is noteworthy that, in any case, the elemental distribution of Ru, Cl, and P on the polyformamidine ligand network is still very homogeneous as evidenced by EDX mapping measurements.

In summary, we have demonstrated the ruthenium-catalysed decomposition of formic acid to yield hydrogen applying a ruthenium complex modified polyformamidine network as a solid catalyst. The polyformamidine acts as a dual support: on



**Fig. 6** SEM micrographs and EDX mapping of *in situ* synthesized Ru&PPh<sub>3</sub>@PF (4) powder after catalysis.

the one hand as a ligand and on the other hand as a base for the activation of formic acid. Future studies will be directed to the synthesis of more basic polyamines to increase the reactivity of the system.

## Experimental section

### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker Avance III 200 spectrometer (<sup>1</sup>H: 200.13 MHz; <sup>13</sup>C: 50.29 MHz) using the proton signals of the deuterated solvents as reference. <sup>13</sup>C{<sup>1</sup>H} CP (cross-polarization)/MAS (magic angle spinning) NMR spectra were recorded on a Bruker Avance 400 spectrometer (<sup>13</sup>C: 100.57 MHz) using a 4 mm double resonance HX MAS probe. The CP spectra were recorded with a cross-polarization time of 2 ms and composite pulse <sup>1</sup>H decoupling was applied during the acquisition. IR spectra were recorded either on a Nicolet Series II Magna-IR-System 750 FTR-IR or on a Perkin Elmer Spectrum 100 FT-IR. Melting points (mp) were determined on a BSGT Apotec II capillary-tube apparatus and are uncorrected.

Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. Powder X-ray diffraction (XRD) measurements were recorded on a Bruker D8 Advanced with CuK<sub>α</sub>-radiation (λ = 0.1546 nm) and scintillator detector. SEM measurements were performed on a JEOL 7401 F equipped with an EDX Bruker Quantax XFlash 4010 Detector.

The contents of Ru and P in the bulk materials have been measured by elemental analysis methods *via* AAS (Ru) with an AAnalyst 300 (Perkin Elmer) and *via* UV/VIS (Lambda 2, Perkin Elmer).

### Synthesis of polyformamidine 2

To a solution of 1,4-benzenediamine (0.43 mol) in DMSO (500 mL) was added triethyl orthoformate (0.87 mol) at room temperature. The solution was stirred at 140 °C for 24 hours. During that time a precipitate was formed. After cooling to room temperature the mixture was treated with acetone



(500 mL) and the precipitate was filtered and washed with acetone. The solid was purified in a Soxhlet extractor using acetone as solvent for 24 hours. The yellow-orange powder was dried in a vacuum at 80 °C for 8 hours. Yield = 82%; mp = >300 °C;  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS NMR (100 MHz)  $\delta$  = 146.4 (br), 133.1 (br), 140.2 (br), 124.1 (br), 120.4 (br), 117.8 (br), 115.4 (br) ppm; IR (KBr):  $\tilde{\nu}$  = 2917 (w), 2857 (w), 1665 (s), 1637 (s), 1498 (s), 1308 (m), 1205 (m), 982 (m), 820 (m), 526 (m)  $\text{cm}^{-1}$ ; elemental analysis: anal. calcd for  $\text{C}_7\text{H}_6\text{N}_2$  (based on repeating unit) (%): C: 71.17, H: 5.12, N: 23.71. Found: C: 67.21, H: 5.25, N: 22.89%.

### Synthesis of ruthenium supported on polyformamidine (3)

A suspension of  $[\text{RuCl}_2(p\text{-cymene})]_2$  (0.36 mmol) and polyformamidine 2 (1.0 g) in THF (50 mL) was refluxed for 18 hours. The volatiles were removed in a vacuum and the residue was purified in a Soxhlet extractor using acetone as solvent for 24 hours. The red-brown powder was dried in a vacuum at 80 °C for 8 hours. Ru@PF:  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS NMR (100 MHz)  $\delta$  = 244.7 (br), 233.8 (br), 219.9 (br), 145.5 (br), 139.3 (br), 133.2 (br), 124.4 (br), 120.9 (br), 118.1 (br), 115.5 (br), 99.5 (br), 80.9 (br), 33.3 (br), 27.8 (br), 25.0 (br), 20.7 (br); IR (KBr):  $\tilde{\nu}$  = 3032 w, 2945 w, 2870 w, 1663 s, 1503 s, 1409 w, 1309 s, 1208 m, 984 w, 822 m, 528  $\text{cm}^{-1}$ ; elemental analysis: found: C: 60.14, H: 5.12, N: 14.78%.

### Synthesis of ruthenium supported on polyformamidine and addition of $\text{PPh}_3$ (4)

A suspension of 3 (100 mg) and triphenylphosphane (0.072 mmol) in THF (50 mL) was refluxed for 18 hours. Afterwards the volatiles were removed in a vacuum and the obtained red-brown powder was dried in a vacuum at 80 °C for 8 hours. Ru&PPh<sub>3</sub>@PF:  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS NMR (100 MHz)  $\delta$  = 243.9, 232.5, 219.3, 160.5, 144.5, 137.9, 136.0, 132.4, 123.5, 119.8, 117.1, 114.1, 87.9, 60.6, 44.8, 32.7, 29.7, 25.7, 20.8, 17.6;  $^{31}\text{P}\{^1\text{H}\}$  CP/MAS NMR  $\delta$  = 33.4 ppm; IR (KBr):  $\tilde{\nu}$  = 3400 w, 3048 w, 2940 w, 2868 w, 1663 s, 1504 s, 1408 w, 1310 m, 1229 w, 1209 m, 1116 w, 1035 w, 985 w, 822 w, 752 w, 696 w, 649 w, 527  $\text{cm}^{-1}$ ; elemental analysis: found: C: 65.22, H: 5.37, N: 14.10%.

### Catalytic reactions

All catalytic experiments were carried out under an inert gas atmosphere (argon) with exclusion of air. The substrates were dried by standard laboratory methods prior to use. The formic acid to amine ratio was determined by  $^1\text{H}$  NMR spectroscopy on a Bruker Avance 300 spectrometer. The catalyst precursor  $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$  was purchased from Aldrich. The amount of gas liberated was measured by a gas burette. In addition, a GC for analyzing gases was applied (Agilent 6890N, permanent gases: Carboxen 1000, TCD, external calibration; amines: HP Plot Q, 30 m, FID), and in a few cases an additional hydrogen sensor (Hach Ultra Analytics GmbH) was used for analysis of hydrogen. Blank experiments without a catalyst revealed a volume increase of  $\leq 1$  mL. Typically, the standard deviation for the volumetrically determined hydrogen volumes and calculated activities is between 1 and 10%.

### Ru&PPh<sub>3</sub>@PF (4) after catalysis

IR (KBr):  $\tilde{\nu}$  = 3201 w, 3047 w, 2932 w, 2863 w, 1958 w, 1664 s, 1505 s, 1435 w, 1407 w, 1309 m, 1229 w, 1209 m, 1116 w, 1092 w, 983 w, 905 w, 822 w, 747 w, 722 w, 695 w, 661 w, 540 w, 526  $\text{cm}^{-1}$ ; elemental analysis: found: C: 68.42, H: 5.10, N: 15.99%.

### Acknowledgements

This work was supported by the Cluster of Excellence "Unifying Concepts in Catalysis" (sponsored by the Deutsche Forschungsgemeinschaft and administered by the Technische Universität Berlin), the state of Mecklenburg-Vorpommern and, the BMWi (IGF 16634 BG).

### Notes and references

- 1 *Hydrogen as a Future Energy Carrier*, ed. A. Züttel, A. Borgschulte and L. Schlapbach, Wiley VCH, Weinheim, 2008.
- 2 V. Balzani, A. Credi and M. Venturi, *ChemSusChem*, 2008, **1**, 26–58.
- 3 (a) A. W. C. van den Berg and C. O. Areán, *Chem. Commun.*, 2008, 668–681; (b) J. Graetz, *Chem. Soc. Rev.*, 2009, **38**, 73–82; (c) I. Cumalioglu, A. Ertas, Y. Ma and T. Maxwell, *J. Fuel Cell Sci. Technol.*, 2008, **5**, 034001-1–034001-10; (d) L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353–358; (e) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem.*, 2005, **117**, 4748–4758; *Angew. Chem., Int. Ed.*, 2005, **44**, 4670–4679; (f) M. E. Bluhm, M. G. Bradley, M. R. Butterick III, U. Kusari and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 7748–7749; (g) G. Walker, *Solid-State Hydrogen Storage*, 2008, 3–17; (h) F. Schüth, B. Bogdanovic and M. Felderhoff, *Chem. Commun.*, 2004, 2249; (i) S. Kalinichenka, L. Röntzsch and B. Kieback, *Int. J. Hydrogen Energy*, 2009, **34**, 7749.
- 4 (a) S. Enthaler, *ChemSusChem*, 2008, **1**, 801–804; (b) F. Joó, *ChemSusChem*, 2008, **1**, 805–808; (c) S. Enthaler, J. von Langermann and T. Schmidt, *Energy Environ. Sci.*, 2010, **3**, 1207–1217; (d) B. Loges, A. Boddien, F. Gärtner, H. Junge and M. Beller, *Top. Catal.*, 2010, **53**, 902–914; (e) S. Enthaler and B. Loges, *ChemCatChem*, 2012, **4**, 323–325; (f) M. Grasmann and G. Laurenczy, *Energy Environ. Sci.*, 2012, **5**, 8171–8181.
- 5 (a) A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge and M. Beller, *Angew. Chem.*, 2011, **123**, 6535–6538; *Angew. Chem., Int. Ed.*, 2011, **50**, 6411–6414; (b) G. Papp, J. Csorba, G. Laurenczy and F. Joó, *Angew. Chem., Int. Ed.*, 2011, **44**, 10433–10435; (c) Y. Himeda, S. Miyazawa and T. Hirose, *ChemSusChem*, 2011, **4**, 487–493; (d) R. Tanaka, M. Yamashita, L. W. Chung, K. Morokuma and K. Nozaki, *Organometallics*, 2011, **30**, 6742–6750.
- 6 (a) R. S. Coffey, *Chem. Commun.*, 1967, 923–924; (b) D. Forster and G. R. Beck, *J. Chem. Soc. D*, 1971, 1072; (c) T. Yoshida, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 3941–3942; (d) S. H. Strauss, K. H. Whitmire and D. F. Shriver, *J. Organomet. Chem.*, 1979, **174**, C59–C62; (e) R. S. Paonessa

- and W. C. Trogler, *J. Am. Chem. Soc.*, 1982, **104**, 3529–3530; (f) J. H. Shin, D. G. Churchill and G. Parkin, *J. Organomet. Chem.*, 2002, **642**, 9–15; (g) J.-C. Tsai and K. M. Nicholas, *J. Am. Chem. Soc.*, 1992, **114**, 5117–5124; (h) R. M. Laine, R. G. Rinker and P. C. Ford, *J. Am. Chem. Soc.*, 1977, **99**, 252–253; (i) Y. Gao, J. Kuncheria, G. P. A. Yap and R. J. Puddephatt, *Chem. Commun.*, 1998, 2365–2366; (j) Y. Gao, J. K. Kuncheria, H. A. Jenkins, R. P. Puddephatt and G. P. A. Yap, *J. Chem. Soc., Dalton Trans.*, 2000, 3212–3217; (k) C. Fellay, P. Dyson and G. Laurenczy, *Angew. Chem., Int. Ed.*, 2008, **47**, 3966–3968; (l) C. Fellay, N. Yan, P. J. Dyson and G. Laurenczy, *Chem.–Eur. J.*, 2009, **15**, 3752–3760; (m) S. Fukuzumi, T. Kobayashi and T. Suenobu, *ChemSusChem*, 2008, **1**, 827–834; (n) D. J. Morris, G. J. Clarkson and M. Wills, *Organometallics*, 2009, **28**, 4133–4140.
- 7 (a) B. Loges, A. Boddien, H. Junge and M. Beller, *Angew. Chem.*, 2008, **120**, 4026–4029; *Angew. Chem., Int. Ed.*, 2008, **47**, 3962–3965; (b) A. Boddien, B. Loges, H. Junge and M. Beller, *ChemSusChem*, 2008, **1**, 751–758; (c) B. Loges, A. Boddien, H. Junge, J. R. Noyes, W. Baumann and M. Beller, *Chem. Commun.*, 2009, 4185–4187; (d) A. Boddien, B. Loges, H. Junge, F. Gärtner, J. R. Noyes and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 2517–2520; (e) A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 8924–8934; (f) A. Boddien, F. Gärtner, R. Jackstell, H. Junge, A. Spannenberg, W. Baumann, R. Ludwig and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 8993–8996; (g) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, **333**, 733–736.
- 8 For a base free system see: J. D. Scholten, M. H. G. Precht and J. Dupont, *ChemCatChem*, 2010, **2**, 1265–1270.
- 9 X. Li, X. Ma, F. Shi and Y. Deng, *ChemSusChem*, 2010, **3**, 71–74.
- 10 (a) S. Enthaler, K. Schröder, S. Inoue, B. Eckhardt, K. Junge, M. Beller and M. Driess, *Eur. J. Org. Chem.*, 2010, 4893–4901; (b) K. Schröder, S. Enthaler, B. Join, K. Junge and M. Beller, *Adv. Synth. Catal.*, 2010, **352**, 1771–1778.
- 11 S. Enthaler, S. Krackl, J. D. Epping, B. Eckhardt, S. M. Weidner and A. Fischer, *Polym. Chem.*, 2012, **3**, 751–756.
- 12 (a) M. Rillich, D. Jehnichen, H. Komber and F. Böhme, *Macromol. Chem. Phys.*, 1995, **196**, 1635–1644; (b) F. Böhme, M. Rillich and H. Komber, *Macromol. Chem. Phys.*, 1995, **196**, 3209–3216; (c) M. Rillich, H. Komber and F. Böhme, *Polym. Bull.*, 1993, **31**, 381–385; (d) M. Rillich, L. Häussler, D. Jehnichen and F. Böhme, *Polym. Bull.*, 1995, **34**, 43–48; (e) M. Rillich, L. Häussle, H. Komber, F. Wittig and F. Böhme, *Polym. Bull.*, 1994, **33**, 397–404; (f) H. Komber, C. Klinger and F. Böhme, *Macromolecules*, 1997, **30**, 8066–8068; (g) C. Kunert, D. Voigt, P. Friedel, H. Komber and F. Böhme, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 1280–1287; (h) F. Böhme, C. Klinger and C. Bellmann, *Colloids Surf., A*, 2001, **189**, 21–27.
- 13 H. Junge, A. Boddien, F. Capitta, B. Loges, J. R. Noyes, S. Gladiali and M. Beller, *Tetrahedron Lett.*, 2009, **50**, 1603–1606.
- 14 (a) K. Hirano, S. Urban, C. Wang and F. Glorius, *Org. Lett.*, 2009, **11**, 1019–1022; (b) W. Eul and G. Gattow, *Z. Anorg. Allg. Chem.*, 1986, **535**, 148–158.
- 15 See for instance: A. A. Batista, M. O. Santiago, C. L. Donnici, I. S. Moreira, P. C. Healy, S. J. Berners-Price and S. L. Queiroz, *Polyhedron*, 2001, **20**, 2123–2128.
- 16 See for example: (a) A. Boddien, B. Loges, H. Junge and M. Beller, *ChemSusChem*, 2008, **1**, 751–758; (b) B. Loges, H. Junge, B. Spilker, C. Fischer and M. Beller, *Chem. Ing. Tech.*, 2007, **79**, 741–753; Analogous equipment is used also for the measurement of gas consumption in hydrogenation reactions. This equipment has been developed at the Leibniz-Institut für Katalyse e.V. Rostock together with MesSen Nord and has been described elsewhere, H.-J. Drexler, A. Preetz, T. Schmidt and D. Heller, in *The Handbook of Homogeneous Hydrogenation*, ed. J. G. De Vries and C. J. Elsevier, Wiley-VCH, Weinheim, 2007, vol. 1, pp. 257–293.